California Environmental Protection Agency
AIR RESOURCES BOARD

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Sampling Protocol for Chlorthal-Dimethyl (Dacthal) Application Study

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1.0 Introduction

The California Department of Pesticide Regulation's (DPR) memorandum dated January 28, 2011, "Proposed Toxic Air Contaminant Monitoring For 2011", requests that the Air Resources Board (ARB) conduct a comprehensive air monitoring study for the herbicide Chlorthal-Dimethyl (DCPA) during a ground application.

This study will consist of five sampling periods.

1) A background sample period duration time minimum 12 hours (arrival Tuesday)
2) An application sampling period begins Wednesday morning prior to application and is removed one (1) hour before sunset.
3) A post application overnight sampling period begins Wednesday evening one (1) hour before sunset and is removed one (1) hour after sunrise Thursday morning.
4) A post application daytime sampling period begins Thursday morning one (1) hour after sunrise and is removed one (1) hour before sunset.
5) A post application overnight sampling period begins Thursday evening one (1) hour before sunset and is removed one (1) hour after sunrise Friday morning.

The background sampling period will be performed twelve to twenty-four hours prior to the application of DCPA. The application sampling period will begin thirty minutes prior to the application of DCPA. There will be a total of 62 resin sorbent tube samples eight (8) background, five (5) collocated, five (5) field spikes, one (1) trip spike, one (1) trip blank, 32 application/post application and ten (10) spares.

Background sampling will be started the day before the application and end approximately one (1) hour prior to the start of the application or when the elapsed time reaches a minimum of 12 hours. Eight (8) background samplers will be placed around the perimeter of the field along with one (1) collocated sampler and one (1) field spike sampler on the downwind side.

2.0 Project Goals and Objectives

The primary goal of this monitoring project is to measure the concentrations of DCPA in the ambient air during and after application.

To achieve the project goal, the following objectives should be met:

1. Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.

2. Appropriate application of sampling/monitoring equipment to determine DCPA concentrations in the air adjacent to the application.

3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.

4. A final report containing all relevant information, data and results gathered in the course of MLD's activities during the planning and execution of this project.

3.0 Contacts

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4.0 Study Location

A DCPA application is planned for March 28, 2011 in the Monterey County. The field is located 2 miles south of Salinas on the east side of Highway 101.

5.0 Study Design

The DCPA sampling schedule is listed in Table 1 (Sampling Periods). For March 28, 2011 sunrise occurs at 0659 PST and sunset occurs at 1925 PST.

Due to the State of California's current furlough and overtime policies one (1) day and one (1) night of sampling will be removed from the recommended sampling schedule provided by the California Department of Pesticide Regulations.

TABLE 1: SAMPLING PERIODS

Sample Period Begins	Sample Duration/Event Time
Background (Sunday Arrival)	Minimum 12-24 hours (Pre-Application)
Application (8 PST Monday Morning)	Sample is removed one (1) hour before sunset (Application)
Post application (Monday Evening)	Sample is installed one (1) hour before sunset (Overnight)
Post application (Tuesday Morning)	Sample is installed one (1) hour after sunrise (Daytime)
Post application (Tuesday Evening)	Sample is installed one (1) hour before sunset (Overnight)

a) Background sampling will start the day before the application for a minimum of twelve hours, but no more than twenty four hours. The background samples will be removed at least one (1) hour prior to the start of the application. The background samplers will be installed at all four corners and at each of the four sides of the field at quarterly lengths with one (1) field spike sampler and one (1) collocated sampler next to the downwind site for a total of ten (10) samplers. The field spike samples will be pre-spiked with a concentration of 0.6 micrograms of DCPA.

b) The application sampling period will start approximately thirty minutes prior to the ground application of DCPA and will continue until one (1) hour before sunset. A post application overnight sampling period will start one (1) hour before sunset and continue until one (1) hour after sunrise. A second post application daytime sampling period will start one (1) hour after sunrise and will continue until one (1) hour before sunset. A third post application overnight sampling period will start one (1) hour before sunset and will continue until one (1) hour after sunrise.

c) There will be eight (8) sampling sites around the orchard. For a square field, four (4) sites will be located at each corner and four (4) sites will be located at quarterly lengths on each side. The projected downwind site will have two additional samplers, one (1) collocated and one (1) field spike, located within 0.6

meters of the primary sampler. All sampler intakes will be 1.7 meters (67 ± 6 inches) above the ground. Samplers will be placed 20 ±10 meters (33 to 98 feet) from the edge of the field.

d) Each sample will be collected by passing a measured volume of ambient air through one XAD resin sorbent tube that is mounted on a sampling tree as shown in Figure 1. Sample flow is controlled by an inline rotameter (flow range of 0-5 LPM) and the resin sorbent tube will be protected from direct sunlight or rain. Prior to each sampling period, the sampler is checked for leaks. After the sample resin sorbent tube is installed, the flow rate will be set at 3.0 lpm using a digital mass flow meter. The flow rate will be checked at the end of each sampling period and the average of the start and stop flows shall be 3.0 lpm ±20%. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed and placed in a dry ice cooler. The field log sheet and resin sorbent tube label will contain the following information: log #, sample name, sampler ID number, start and end date/time, start/end elapsed time meter reading, start/end mass flow meter display reading, comments (if applicable), weather conditions and the start/end initials of the operator. The exposed XAD-2 resin sorbent tubes (SKC #226-30-06) with 400 and 200 mg of packing are stored in an ice chest (on dry ice) or in a freezer until extracted in the laboratory.

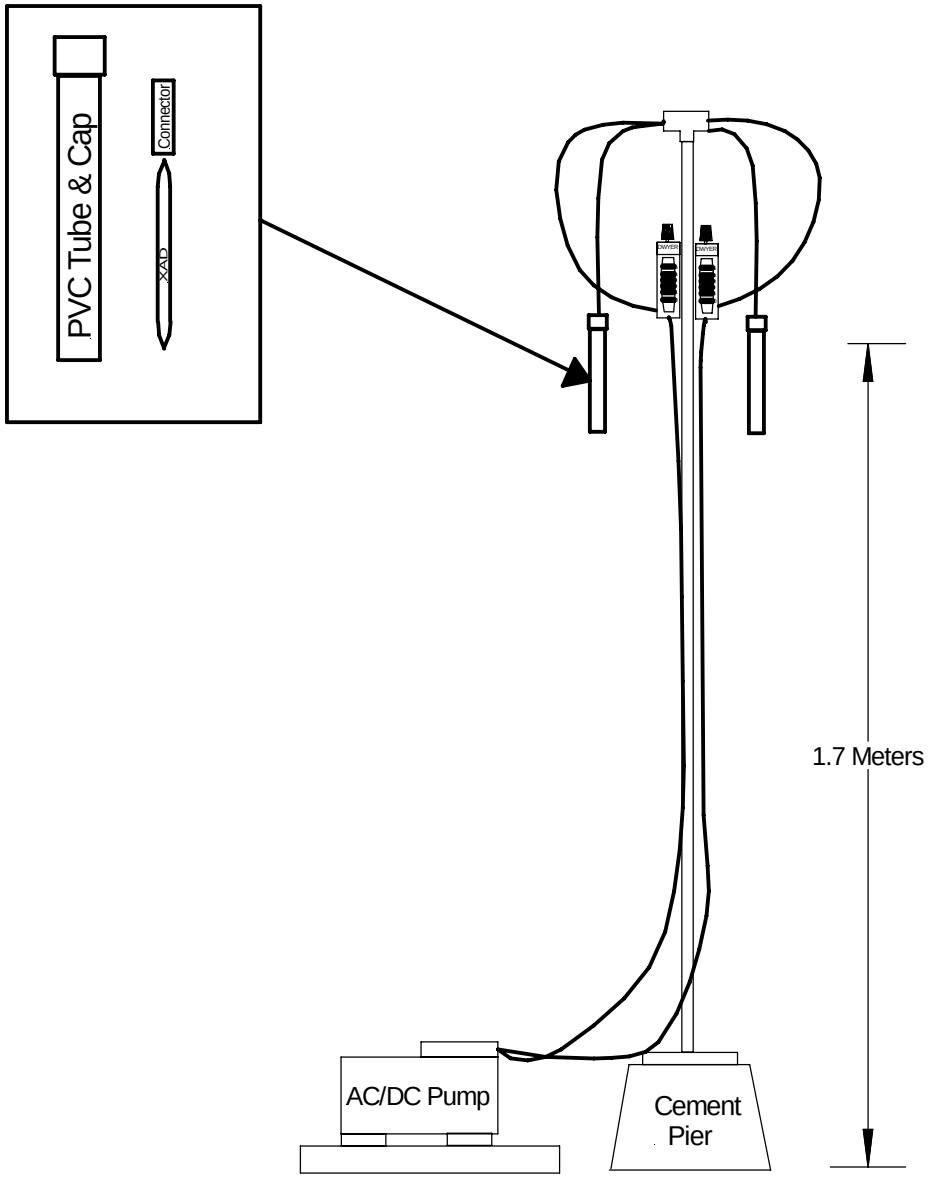

FIGURE 1: AIR SAMPLER TREE WITH PUMP

e) In order to reduce direct exposure to ARB staff during the pesticide application period all samplers will begin a minimum of thirty minutes prior to the start of the application. At the end of each sampling period the following general procedure will occur at each site; flows will be verified, documentation completed, all resin sorbent tubes removed, the battery replaced, a new resin sorbent tube installed and flows adjusted if necessary. Field notes and observations will be recorded (such as DCPA application flow rate and total amount of DCPA applied).

f) Meteorological data will be collected using a Met-One Automet portable meteorology system. The Automet will be located no closer than twenty meters from the edge of the field being monitored. The meteorological sensors will be installed between 5.9 and 6.9 meters above the ground. The AutoMet station will continuously measure and record 5 minute averages for wind speed, wind

direction, ambient temperature and percent relative humidity throughout the background and application sampling periods.

g) The MLD will provide DPR with a final report containing all relevant information, collected data and analytical results gathered during the course of the study.

6.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) staff will hand-carry resin sorbent tubes to and from MLD's laboratory in Sacramento, and to and from the sampling location. The resin sorbent tubes will not be exposed to extreme conditions or subjected to rough handling that might cause loss or degradation of sample. At the end of the each sampling period, all resin sorbent tubes will be removed from the sampler, placed in a culture tube, labeled, and secured in a dry ice cooler.

At each sampling site, the operator will replace the batteries for each pesticide sampler with charged batteries; install a new resin sorbent tube and install the rain/sun shield over the resin tube. The resin sorbent tube field log sheet (See Figure 2) shall be filled out a long with the resin sorbent tube label. Prior to any sampling, flows will be set to 3.0 $\pm$ 0.1 lpm. At the start of each sampling period, the pesticide samplers will be manually turned on and the start date, time, elapsed time meter reading and indicated flow rate will be recorded. At the end of each sampling period, the flow rate will be measured, the pesticide sampler manually shut off and the following recorded on the resin sorbent tube field log sheet; end date, time, elapsed time meter reading and flow.

Sampling will occur as scheduled unless ambient conditions at the start include rain or instantaneous gusts of wind over ten (10) miles per hour. All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will supply Special Purpose Monitoring with 62 resin sorbent tubes; eight (8) backgrounds, five (5) collocated, five (5) field spikes, one (1) trip spike, one (1) trip blank, 32 application/post application and ten (10) spares. A label will be affixed around the top section of the resin sorbent tube identifying the sample. Spikes and other QC resin sorbent tubes will be identified. The NLB will perform analyses for DCPA on all collected samples and report results to SPM in electronic format (Excel) and hardcopy. Laboratory analysis will be performed in accordance with the draft standard operating procedures, "Standard Operating Procedure Sampling and Analysis of Clorthal-Dimethyl (DCPA)." The current analytical Method Detection Limit (MDL) is 100 nanograms (ng) per sample for DCPA. The laboratory's operating procedure is included in this Protocol as Appendix A.

The following resin sorbent tube validation and analytical quality control criteria will be followed during pesticide analysis.

1. **Sample Hold Time**: Sample hold time criteria will be consistent with the laboratory's operation procedure stated 28 days.

2. **Duplicate Analysis**: Laboratory to provide duplicate analytical results and the corresponding relative percent difference (RPD)

3. **Method Detection Limit (MDL)**: Sample analysis results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions (dilution factor will be included in the report)

4. **Analytical Linear Range**: Analytical results greater than 10% of the highest calibration standard shall be diluted and reanalyzed within the calibrated linear range.

7.0 List of Field Equipment

Quantity	Item Description
(1)	Met-One Automet portable meteorology system consisting of a data logger and calibrated sensors measuring 5 minute averages for wind speed, direction, ambient temperature, and relative humidity.
(1)	Measuring Wheel
(1)	200 foot measuring tape
(1)	Tripod and compass
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Aalborg certified mass flow meter 0-5 lpm
(70)	Resin sorbent tubes (8 backgrounds, 5 collocated, 5 field spikes, 1 trip spike, 1 trip blank, 32 application/post application and 10 spares)
(10)	Pesticide sampler each equipped with one (1) each sampling train and voloflows setup to sample one (1) resin tube.
(12)	Pump, 12 VDC.
(80)	Battery, 12 VDC 40 amps.
(13)	Chargers

8.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST) traceable transfer standards will be used to calibrate meteorological sensors and measure sample flow rates.

The sample flow rate of the pesticide sampler's voloflows will be measured using certified mass flow meters with a range of 0-5 liters per minute.

The metrological sensors will be calibrated and aligned following the procedures outlined in the standard operating procedures on the Air Monitoring Web Manual at the following link.

http://arb.ca.gov/airwebmanual/amwmn.php?c=5&t=sop

A label will be affixed around the top section of the resin sorbent tube identifying the sample with the following information: log #, sample name, sampler ID number, start and end date and time, start and end elapsed time meter (ETM) reading, start and end mass flow meter display reading and operators initials.

Collocated (side-by-side) air samplers will operate at one site during the study period. This collocated site will be located at the projected downwind site.

Field Spike (FS): Eight (5) field spikes will be prepared by the laboratory by injecting resin sorbent tubes with a known concentration of DCPA. The field spike resin sorbent tubes will be coupled with a pesticide sampler and collocated next to the projected downwind sampler. One (1) each field spike will be collected during each sampling period.

Trip Spike (TS): A trip spike will be prepared by the laboratory by injecting a resin sorbent tube with a known concentration of DCPA with the same level as the field spikes. The trip spike resin sorbent tube accompanies the sample resin sorbent tubes from the lab to the field but is not sampled.

Trip Blank (TB): A trip blank will be prepared by the field staff. The trip blank resin sorbent tube accompanies the sample resin sorbent tubes from the lab to the field and returns but is not sampled.

Collocated (C): Collocated samples will be collected at the designated down wind sampling site during all sampling periods starting with the background period.

Valid samples are those that have a final corrected average flow within $\pm$ 20% of 3.0 lpm.

Site/Sample Identification

The DCPA application sampling sites will be named accordingly for the background, ambient, application, and post application as follows:

Background Site Naming:

BKG-NE-1
BKG-NE-C
BKG-NE-FS-1

Application Site Naming:

NE-1	NE-1C	NE-1FS
SE1-1	SE2-1	
SW1-1	SW2-1	
NWC-1	NEC-1	
SEC-1	SWC-1	

Letter Abbreviations as follows

N = North Side
S = South Side
W = West Side
E = East Side
BKG = Background Sample
FS = Field Spike
C = Co-located
NEC = NE Corner Sample
NWC = NW Corner Sample
SEC = SE Corner Sample
SWC = SW Corner Sample
TS = Trip Spike
TB = Trip Blank
FB = Field Blank

Following the quality control procedures listed above will ensure the quality and integrity of the samples collected in the field and will insure accurate field and laboratory results.

9.0 Deliverables

9.1 Northern Laboratory Branch (NLB) Deliverables

Within 90 days after the last collected sample is received at the laboratory, the NLB will provide SPM with a report that will include the following topics:

1) Table(s) of sample to include:
   a. Sample identification (name).
   b. Date sample received from field.
   c. Date sample analyzed.
   d. Dilution ratio.
   e. Analytical results.
2) All equations used in calculating analytical results.
3) Table of duplicate results including calculated relative percent difference (RPD) when applicable.
4) Table of collocated results.
5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries when applicable.
6) Table of analytical results from all trip blanks.
7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries when applicable.
8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.
9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

9.2 Air Quality Surveillance Branch Deliverables

Within 90 days from receipt of the final results report from the NLB, AQSB will provide DPR with a report containing the following topics:

1) Sampling Protocol.
2) Personnel Contact List.
3) Site Maps.
4) Site Photographs.
5) Site Descriptions and Measurements (site, sampler, GPS coordinates, inlet height, distance to roads, site-specific comments, DCPA application rate, and total pounds or gallons of DCPA applied).
6) Sample Summary Table.
7) Field Log Sheets.
8) Laboratory Analysis Reports with calculations in electronic format.
9) Met Station and Sampler Calibration Reports.
10) Transfer Standards' Certification Reports.
11) Disk containing electronic files of 5-minute averaged Meteorological Data.
12) Disk containing electronic files of Report.

XAD-2 RESIN SORBENT TUBE FIELD LOG SHEET

Project: DCPA Pesticide Application Air Monitoring

Start Flow Set: 3.0 ±0.1 lpm End Flow Criteria: 3.0 lpm ±20%

Log #	Sample Name	Sampler ID Number	Date & Time Entry Example (6/14/08 13:42)		Elapsed Time Meter (ETM)		Mass Flow Meter Display		Corrected Average Flow	Comment Number	Weather K,P,C,F&R		Initials	
			Start	End	Start	End	Start	End			Start	End	Start	End

MFM Used #: _____ **Slope:** _____ **Intercept:** _____

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog and R = Rain (any)

Figure 2: Resin Sorbent Tube Field Log Sheet

APPENDIX A: Standard Operating Procedure Sampling and Analysis of Chlorthal-Dimethyl (DCPA).

The Special Analysis Section of MLD's Northern Laboratory Branch will perform the analyses for DCPA collected by the resin sorbent tube method. This analytical procedure is entitled, "Standard Operating Procedure Sampling and Analysis of Chlorthal-Dimethyl (DCPA)" and can be located starting on the next page.